Tripodal Amides Containing a Totally Silicon-Based Ligand Framework

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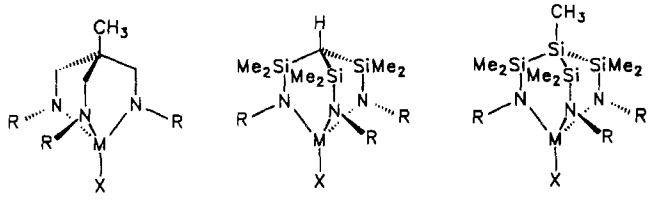
A novel type of tripodal amido ligand with a totally silicon-based (trisilylsilane-derived) ligand framework has been synthesized and coordinated to tetravalent titanium and zirconium. The key compound in the ligand synthesis is the chlorosilane $H_3CSi\{Si(CH_3)_2Cl\}_3$ (**2**) which upon condensation with a range of primary amines $R-NH_2$ (R = aryl, alkyl) yields the amino-functionalized ligand precursors $H_3CSi\{Si(CH_3)_2NHR\}_3$ (**3a–e**). Their corresponding trilithium salts have been found to be the appropriate amide transfer reagents in the subsequent syntheses of the transition metal complexes. Single-crystal X-ray structure analyses of the trilithium triamide $H_3CSi\{Si(CH_3)_2N(Li)tBu\}_3$ (**4a**) and the Ti complex $H_3CSi\{Si(CH_3)_2N(p\text{-}Tol)\}_3TiBr$ (**5b**) have established their respective adamantane- and [2.2.2]bicyclooctane-related cage structures.

Polydentate amido ligands co-ordinated to high-valent transition metal atoms have provided the key to the stabilization of a wide range of molecular fragments and structural units at the metal which have been thought to be inherently labile[1,2]. They may even effect the complete shielding of an otherwise highly reactive co-ordination site[3]. Most of the work has thus far focussed upon the first-row transition elements[1,3,4]. However, there are ever-increasing efforts to extend the use of such ligand systems to the co-ordination chemistry of the heavier transition elements[5]. One of the keys to a successful implementation of this synthetic goal is the availability of polydentate amido ligands with "metal-binding sites" of the appropriate size.



A **B** **C**

M = tetravalent early transition metal, X = Halide

For example, the polydentate ligands in **A** and **B**[6,7] have been found to act as ideal chelating ligands for tetravalent titanium[8] (as well as vanadium[9]) complexes but to give poor results with the heavier group-4 metals. As this is probably due to a "mismatch" between the size of the binding site of the amido ligand and the ionic diameter of the central metal atom, a more open, but equally stable ligand system designed for the heavier early transition elements appeared desirable. With this aim we have extended the series to include a new class of amido tripods which for the first time contain a totally silicon-based ligand framework (Type **C**). The increasing bond lengths (C–C < C–Si < Si–Si) in the ligand framework on going from the carbon-based ligands (**A**) to the trisilylmethane-derived ligands (**B**) and then to the trisilylsilane-derived systems provide a straightforward way of controlling the size of the metal-binding cavity. In this paper we report the synthesis of a new class of amino-functionalized trisilylsilanes, the structural characterization of an adamantoidal lithium amide transfer reagent and the use of these new types of amido tripods in the synthesis of monofunctional titanium and zirconium amido halides.

Results and Discussion

A. Syntheses of the Amino-Functionalized Trisilylsilanes and their Conversion to the Corresponding Trilithium Triamides

The amine precursors of the ligands may be conveniently obtained from the known silane $H_3CSi[Si(CH_3)_3]_3$ (**1**)[10,12], which was first synthesized by Gilman and coworkers by cleavage of $Si[Si(CH_3)_3]_4$ with MeLi and subsequent methylation of the in situ-generated anion $[Si\{Si(CH_3)_3\}_3]^-$ with trimethyl phosphate. We have chosen the direct route by reductive coupling of CH_3SiCl_3 with $(CH_3)_3SiCl$ in the presence of lithium which gives the desired silane **1** in ca. 60% yield (Eq. 1)[11].

$$CH_3SiCl_3 + 3(CH_3)_3SiCl \xrightarrow[THF]{Li} \underset{\mathbf{1}}{CH_3Si[Si(CH_3)_3]_3} + 6LiCl \quad (1)$$

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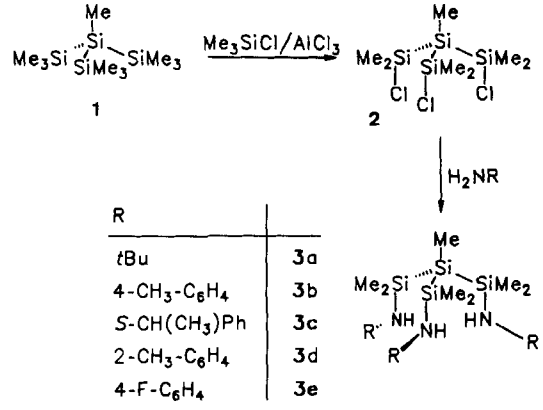
Compound **1** is converted to the silyl halide **2** by $AlCl_3$-catalyzed Cl/CH_3 exchange with $(CH_3)_3SiCl$ (Scheme 1), a method pioneered by Ishikawa et al. for the functionalization of, in particular, linear polysilanes[13]. Similar to the key precursor $HC[Si(CH_3)_2Br]_3$[7,14] in the chemistry of the amino-functionalized trisilylmethanes which we have reported previously, compound **2** may be condensed with a wide range of primary amines to give the amino-functionalized trisilylsilanes **3a–e**. It is probably due to the steric activity of the methyl group attached to the bridgehead silicon atom in **3a–e** that an equally pronounced conformational variety in solution (adamatoidal and "inverted" conformations) as found for the trisilylmethane derivations has not been observed[8b].

Scheme 1



Similar to the metallation of the corresponding trisilylmethanes[7], lithiation of **3a–c** is a highly co-operative process (as established by ^{7}Li-NMR spectroscopy) yielding the trilithium triamides **4a–d**, which on the basis of their spectroscopic data display an effective threefold molecular symmetry in solution and are thought to have an adamantane-related molecular structure.

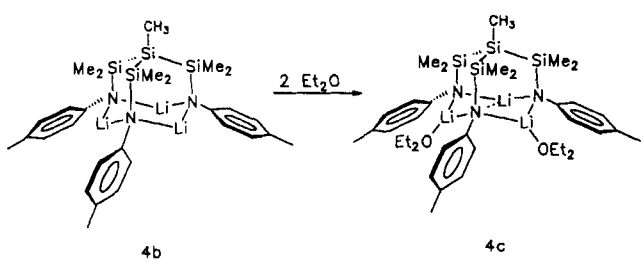
4a $H_3CSi[Si(CH_3)_2N(Li)tBu]_3$

4b $H_3CSi[Si(CH_3)_2N(Li)p\text{-Tol}]_3$

4c $H_3CSi[Si(CH_3)_2N(Li)p\text{-Tol}]_3(Et_2O)_2$

4d $H_3CSi\{Si(CH)_2N(Li)[(S)CH(CH_3)C_6H_5]\}_3$

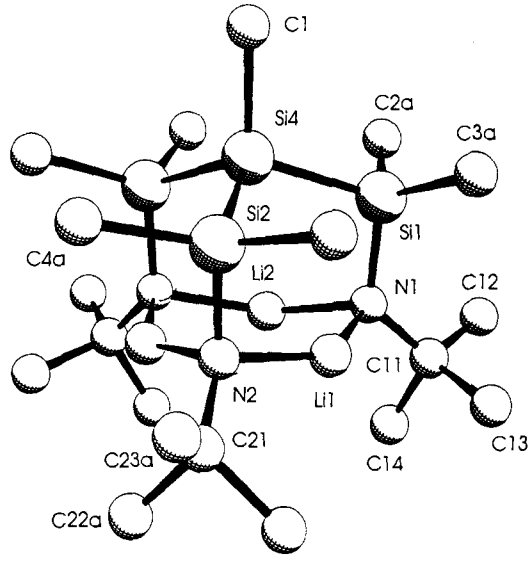
In view of the extreme air and moisture sensitivity and thermal lability of the tolyl-substituted lithium amide **4b**, this reagent is more conveniently handled as its bis-diethyl ether solvate **4c**, which on the basis of the structurally characterized bis-solvate $HC[Si(CH_3)_2N(Li)tBu]_3(THF)_2$ is thought to have a similar "ladder" $(LiN)_3$ array:



B. Crystal Structure Analysis of $CH_3Si[Si(CH_3)_2N(Li)tBu]_3$ (4a)

The postulated solution structure of the trilithium triamides was substantiated by a single-crystal X-ray structure analysis of the *tert*-butyl-substituted amide **4a** (Figure 1).

Figure 1. Molecular structure of **4a** in the crystal. Principal bond lengths [Å] and interbond angles [°]: Si1–Si4 2.351(6), Si2–Si3 2.357(10), Si1–N1 1.71(1), Si2–N2 1.69(2), N1–Li1 1.97(3), N1–Li2 1.90(2); Si1–Si4–Si1′ 110.1(3), Si2–Si4–Si1 110.4(2), Li2–N1–Li1 95(1), N2–Li2–N1 139(1), Li1–N2–Li1 96(2)

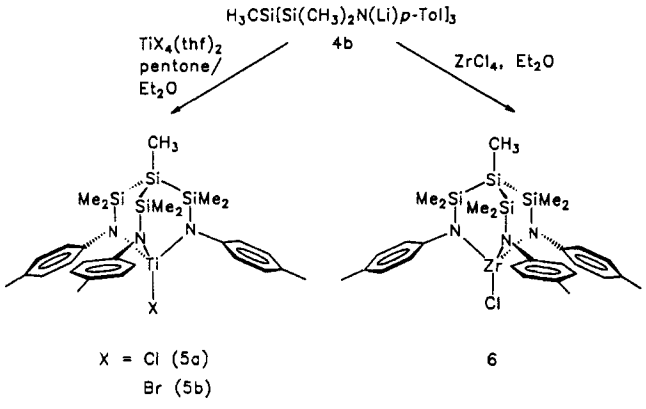


Whereas the structures of the neopentane-derived lithium amides have been found to be dimeric aggregates containing a central $\{LiN\}_6$ cage[6], **4a** crystallizes as isolated monomeric species. Its structural centre piece is the hetero-adamantane cage comprising four silicon (Si1, Si1′, Si2, Si4), three nitrogen (N1, N1′, N2), and three lithium atoms (Li1, Li1′, Li2). The molecule has crystallographic mirror symmetry, the mirror plane being spanned by the atoms C1, Si4, Si2, N2, Li1, C21. In contrast to the situation found in the structure of $[\{(CH_3)_3Si\}_2N(Li)]_3$ which has a planar lithium-nitrogen array[15], the $\{LiN\}_3$ ring is slightly puckered (Li–N–Li′–N′ torsion angles ranging from 30.0 to 42.1°) as a consequence of the bridging methylsilyl function "stitching" the three disilylamine units together and thus forcing them out of the planar arrangement. It should be noted though that the Si–N vectors in **4a** are not parallel to the idealized threefold molecular axis but slightly "cave in" at the N atoms towards the center. Their arrangement [$d(Li-N)_{av}$ = 1.94 Å] appears to be dictated by the almost invariable Li–N distances observed in most related unsolvated lithium amides[16]. Compound **4a** therefore represents the missing link in the systematics of lithium amide structures ranging from the planar trimeric monofunctional amides to the extreme distortions of the ring arrays which are part of the cage structures in $[H_3CC\{CH_2N(Li)R\}_3]_2$[6]. Here as well as in the trisilylmethane analogues[7] shielding by the bulky *tert*-butyl groups prevents aggregation to dimers.

C. Synthesis and Structural Characterization of Ti- and Zr-Amido Complexes Containing the Trisilylsilane-Derived Tripodal Amides

Reaction of the tolyl-substituted lithium amide H_3CSi-$[Si(CH_3)_2N(Li)p\text{-}Tol]_3$ (**4b**) with $TiX_4(thf)_2$ and $ZrCl_4$ yields the transition metal amido complexes $[H_3CSi\{Si(CH_3)_2N(p\text{-}Tol)\}_3MX]$ {M = Ti, X = Cl and Br: **5a** and **5b**, M = Zr, X = Cl: **6**). The effective threefold molecular symmetry of the ligands in the molecules as indicated by the spectroscopic data obtained in solution is consistent with the [2.2.2]bicyclooctane-related cage structures as shown in Scheme 2.

Scheme 2



A single-crystal X-ray structure analysis of the titanium complex **5b** has established the central [2.2.2]bicyclooctane-related cage structure of the amido complexes depicted in Figure 2 along with the principal bond lengths and interbond angles. One of the bridgehead positions is occupied by the Ti–Br fragment. The efficient shielding of the one co-ordination hemisphere of the Ti atom is readily apparent, as is the relatively open environment of the remaining bromide ligand compared to the situation in the structurally characterized azatranes. This is in part a consequence of the conformation the tolyl groups adopt with respect to the amide skeletal geometry, generating an overal "lamp shade" arrangement of the tripodal ligand similar to that found in the trisilylmethane-derived transition metal complexes[1,8b].

A particularly notable feature in the crystal structure of **5b** is the degree to which the amido donor functions have to "cave in" in order to accommodate the small tetravalent titanium atoms. As a consequence, the peripheral tolyl groups are drawn together leading to a decreased size of the "reactive site" occupied by the halide ligand. Apart from the size of the metal binding site discussed above, the choice of the appropriate ligand system among types **A**–**C** for the co-ordination to a particular metal may also influence the size of the remaining co-ordination site in these monofunctional complexes (occupied by the halide) as indicated in Figure 3.

All three amido nitrogen atoms were found to have almost planar geometry as has heen found in virtually all structurally characterized transition metal amido complexes[17].

Figure 2. Molecular structure of **5b** in the crystal. Principal bond lengths [Å] and interbond angles [°]: Ti1–Br1 2.411(3), Ti1–N1 1.915(12), Ti1–N2 1.915(10), Ti1–N3 1.917(12), Si1–Si4 2.348(6), Si2–Si4 2.331(6), Si3–Si4 2.335(6), Si1–N1 1.776(12), Si2–N2 1.777(11), Si3–N3 1.772(12); N3–Ti1–N1 105.6, N3–Ti1–N2 103.6(5), N2–Ti1–N1 103.7(5), N1–Ti1–Br1 114.4(3), N2–Ti1–Br1 115.1(3), N3–Ti1–Br1 113.1(4)

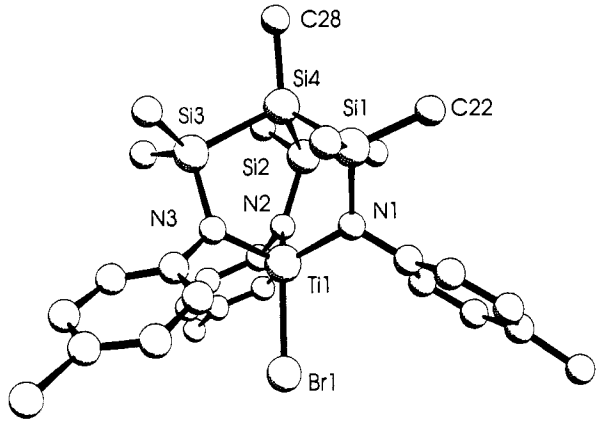
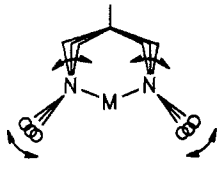


Figure 3. Schematic representation of the influence that the choice of the ligand framework may have upon the size and geometry of the "binding site" in complexes of a given tetravalent metal



Conclusions

This study has established a new type of tripodal amido ligand in transition metal chemistry which complements the neopentane- and trisilylmethane-derived systems developed previously by us. The amino-functionalized trisilylsilanes employed in this work are expected to be particularly useful in the co-ordination chemistry of the heavier early transition elements.

The novel types of "monofunctional" early transition metal amido halides reported here represent a set of building blocks for the generation of directly metal-metal bonded oligonuclear co-ordination compounds. Work aimed at their synthesis and the investigation of their chemical behavior is currently underway.

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Experimental

All manipulations were performed under dried argon in standard (Schlenk) glassware which was flame-dried with a Bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with argon. The deuterated solvents used for the NMR-spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and dried with 4-Å molecular sieves.

^1H, ^7Li, ^{13}C, ^{19}F, ^{29}Si NMR: Bruker AC 200 with a B-VT-2000 variable-temperature unit (at 200.13, 77.88, 50.32, 188.31, and 39.76 MHz, respectively), tetramethylsilane, $CFCl_3$ (ext.), and LiI/H_2O (1 M, external) as references. – IR: Bruker IRS 25 FT. – Elemental analyses: Microanalytical laboratory of the Chemistry Department at Würzburg. – Melting points: Differential thermal analysis. – Compound $CH_3Si[Si(CH_3)_3]_3$ (**1**) was prepared according to the procedure published by Marsmann et al. which is based on the reductive coupling of CH_3SiCl_3 with $(CH_3)_3SiCl$[11]. All other chemicals used as starting materials were obtained commercially and used without further purification.

1) *Preparation of $CH_3Si[Si(CH_3)_2Cl]_3$* (**2**): A mixture of 42.8 g (393.9 mmol) of $(CH_3)_3SiCl$, 9.71 g (36.9 mmol) of **1**, and 1.6 g of aluminium chloride was heated at 70°C oil bath temp. in a round-bottom Schlenk flask equipped with a 40-cm Vigreux column and a distillation bridge. Over a period of 4–6 h the tetramethylsilane generated (9.76 g, 110.7 mmol) distilled out of the reaction mixture. After completion of the conversion excess chlorotrimethylsilane was removed by distillation and the $AlCl_3$ catalyst deactivated by addition of 5 ml of acetone. The reaction product was obtained as a colourless solid after vacuum distillation (b.p. 88°C/0.1 Torr). Yield 10.84 g (91%). – ^1H NMR ($CDCl_3$, 295 K): δ = 0.33 ($SiCH_3$), 0.62 [$Si(CH_3)_2Cl$]. – $^{13}C\{^1H\}$ NMR: δ = –13.4 ($SiCH_3$), 4.5 [$Si(CH_3)_2Cl$]. – IR (KBr): $\tilde{\nu}$ = 2961 cm^{-1} s, 2893 m, 1400 m, 1253 s, 1035 m br, 841 s, 795 s, 779 s, 671 s. – $C_7H_{21}Cl_3Si_4$ (323.9): calcd. C 25.95, H 6.53; found C 26.13, H 6.66.

2) *Preparation of $CH_3Si[Si(CH_3)_2NHtBu]_3$* (**3a**): To a stirred mixture of 15.81 g (261.0 mmol) of *tert*-butylamine and 20 ml of diethyl ether, which was externally cooled with an ice bath, was added a solution of 5.83 g (18.0 mmol) of **2** in 80 ml of diethyl ether over a period of ca. 2 h. After warming to room temp. the colourless suspension was stirred for another 15 h, the solvent removed in vacuo and the residue extracted with 60 ml of pentane. After filtration of the extract through Celite the filtrate was concentrated to 20 ml and stored at –30°C. The reaction product precipitated as large colourless crystals which were isolated by filtration and dried in vacuo. Yield 4.92 g (63%), m.p. 64°C. – ^1H NMR ($CDCl_3$, 295 K): δ = –0.05 ($SiCH_3$), 0.28 [$Si(CH_3)_2N$], 1.16 [$(CH_3)_3C$]. – $^{13}C\{^1H\}$ NMR: δ = –13.6 ($SiCH_3$), 4.6 [$Si(CH_3)_2N$], 34.0 [$(CH_3)_3C$], 51.2 [$C(CH_3)_3$]. – IR (KBr): $\tilde{\nu}$ = 3324 cm^{-1} m, 2956 vs, 2893 s, 1464 m, 1401 m, 1379 s, 1356 s, 1239 s, 1216 s, 1002 s, 841 s, 807 s, 781 vs, 756 s, 705 m, 673 m, 621 w. – $C_{19}H_{51}N_3Si_4$ (434.0): calcd. C 52.58, H 11.84, N 9.68; found C 52.59, H 12.04, N 9.61.

3) *General Procedure for the Preparation of $CH_3Si[Si(CH_3)_2NHR]_3$* (**3b–e**): To a stirred mixture of 50 mmol of the primary amine RNH_2 and 5.6 g of triethylamine in 60 ml of diethyl ether, which was externally cooled with an ice bath, was slowly added a solution of 5.42 g (16.7 mmol) of **2** in 60 ml of diethyl ether. After warming to room temp. the colourless suspension was stirred for another 15 h, the solvent removed in vacuo and the residue extracted with 100 ml of pentane. After filtration of the extract through Celite the filtrate was concentrated to 20 ml and stored at –30°C. The reaction product precipitated as a colourless crystalline solid which was isolated by filtration and dried in vacuo.

$CH_3Si[Si(CH_3)_2NH(4\text{-}CH_3C_6H_4)]_3$ (**3b**): Yield 73%, m.p. 30°C. – ^1H NMR ($CDCl_3$, 295 K): δ = 0.37 (s, $SiCH_3$), 0.40 [s, $Si(CH_3)_2$], 2.24 (s, $C_6H_4CH_3$), 3.35 (s, NH), 6.46 (d, $^3J_{HH}$ = 8.4 Hz, 2,6-H), 6.93 (d, 3,5-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): δ = –10.6 ($SiCH_3$), 1.4 [$Si(CH_3)_2$], 20.3 ($C_6H_4CH_3$), 115.1 (C-4), 116.2 (C-2/6), 129.7 (C-3,5), 144.6 (CN). – IR (pentane): $\tilde{\nu}$ = 3384 cm^{-1} m, 3032 m, 2945 s, 1618 s, 1512 s, 1440 m, 1368 s, 1179 m, 1123 m, 1113 m, 1030 m br, 895 s. – $C_{28}H_{45}N_3Si_4$ (536.0): calcd. C 62.74, H 8.46, N 7.84; found C 63.15, H 9.12, N 7.99.

$CH_3Si\{Si(CH_3)_2NH[(S)\text{-}CH(CH_3)C_6H_5]\}_3$ (**3c**): Yield 42%. – ^1H NMR (C_6D_6, 295 K): δ = 0.15 (s, $SiCH_3$), 0.19, 0.32 [s, $Si(CH_3)_2$], 1.21 (d, $^3J_{HH}$ = 9.4 Hz, CHN*H*), 1.29 (d, $^3J_{HH}$ = 6.6 Hz, $CHCH_3$), 4.05 (m, CH), 7.02–7.28 (m, C_6H_5). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ = –12.7 ($SiCH_3$), 2.0, 2.6 [$Si(CH_3)_2$], 28.4 ($CHCH_3$), 52.6 ($CHCH_3$), 126.1 (C-2), 126.6 (C-4), 128.5 (C-3), 149.5 (CN). – IR (nujol): $\tilde{\nu}$ = 3368 cm^{-1} w br, 3013 m, 2940 vs, 2880 m, 1486 m, 1448 m, 1392 m, 1362 m, 1257 s, 1243 s, 1196 m, 1114 vs, 1026 s, 941 m, 812 vs br, 697 vs. – $C_{31}H_{51}N_3Si_4$ (578.1): calcd. C 64.41, H 8.89, N 7.27; found C 64.37, H 9.27, N 8.03.

$CH_3Si[Si(CH_3)_2NH(2\text{-}CH_3C_6H_4)]_3$ (**3d**): Yield 63%. – ^1H NMR (C_6D_6, 295 K): δ = 0.39 [s, $Si(CH_3)_2$], 0.46 (s, $SiCH_3$), 1.87 (s, $CH_3C_6H_4$), 3.30 (s, NH), 6.74 (ddd, $^3J_{HH}$ = 7.4, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.1 Hz, 5-H), 6.88 (dd, $^3J_{HH}$ = 7.8 Hz, 3-H), 6.96–7.07 (m, 4,6-H). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ = –20.0 ($SiCH_3$), 1.7 [$Si(CH_3)_2$], 17.7 ($CH_3C_6H_4$), 115.4 (C-6), 118.6 (C-4), 124.0 (C-2), 127.4 (C-5), 131.0 (C-3), 145.8 (CN). – IR (pentane): $\tilde{\nu}$ = 3395 cm^{-1} m, 1600 s, 1574 s, 1498 s, 1486 s, 1361 m, 1285 vs, 1243 s, 1104 w, 1045 m, 890 s, 831 s, 790 s, 770 s, 743 vs. – $C_{28}H_{45}N_3Si_4$ (536.0): calcd. C 62.74, H 8.46, N 7.84; found C 62.82, H 8.74, N 8.02.

$CH_3Si[Si(CH_3)_2NH(4\text{-}FC_6H_4)]_3$ (**3e**): Yield 67%. – ^1H NMR (C_6D_6, 295 K): δ = 0.24 [s, $Si(CH_3)_2$], 0.25 (s, $SiCH_3$), 3.07 (s, NH), 6.28–6.33, 6.71–6.80 (m, C_6H_4F). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ = –10.1 ($SiCH_3$), 1.4 [$Si(CH_3)_2$], 116.0 (d, $^2J_{FC}$ = 17.5 Hz, C-2), 117.5 (d, $^3J_{FC}$ = 7.4 Hz, C-3), 143.6 (CN), 156.6 ($^1J_{FC}$ = 235.8 Hz). – $^{19}F\{^1H\}$ NMR (C_6D_6, 295 K): δ = –127.8. – IR (nujol): $\tilde{\nu}$ = 3385 cm^{-1} m, 1605 m, 1498 s, 1466 s, 1356 s, 1285 s, 1245 s, 1215 s, 1152 m, 1095 m, 892 s, 821 s br, 773 s br. – $C_{25}H_{36}F_3N_3Si_4$ (547.9): calcd. C 54.80, H 6.62, N 7.67; found C 54.62, H 6.76, N 7.50.

4) *General Procedure for the Preparation of Trilithium Triamides* (**4a–d**): To a stirred solution of 1.76 mmol of the free amine in 20 ml of pentane which was cooled at –60°C were added 2.11 ml of a solution of 2.5 M *n*-butyllithium in hexanes. After warming to room temp. the reaction mixture was stirred for another 2 h, concentrated to 10 ml, and cooled to –30°C. The unsolvated lithium salts *$CH_3Si[Si(CH_3)_2N(Li)tBu]_3$* (**4a**) *$CH_3Si[Si(CH_3)_2N(Li)(4\text{-}CH_3C_6H_4)]_3$* (**4b**) and *$CH_3Si\{Si(CH_3)_2N(Li)[(S)\text{-}CH(CH_3)C_6H_5]\}_3$* (**4d**) were directly obtained as colourless crystalline solids. Due to its extreme reactivity, **4b** was generally isolated as the bis-diethyl ether adduct which was generated by addition of 1 ml of diethyl ether to the solution of the in situ-prepared amide and subsequent cooling to –30°C upon which *$CH_3Si[Si(CH_3)_2N(Li)(4\text{-}CH_3C_6H_4)]_3(Et_2O)_2$* (**4c**) crystallized as a colourless solid.

4a: Yield 78%, m.p. 45°C (dec.). – ^1H NMR (C_6D_6, 295 K): δ = 0.14 (s, CH_3Si), 0.52 [s, $Si(CH_3)_2$], 1.09 [s, $C(CH_3)_3$]. – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ = –13.4 (CH_3Si), 8.2 [$Si(CH_3)_2$], 37.5 (CH_3), 53.7 [$C(CH_3)_3$]. – $^7Li\{^1H\}$ NMR (C_6D_6, 295 K): δ = 0.47. – $C_{19}H_{48}Li_3N_3Si_4$ (451.9): calcd. C 50.50, H 10.71, N 9.30; found C 50.81, H 11.02, N 9.58.

4b: Yield 51%. – ^1H NMR (C_6D_6, 295 K): δ = 0.13 (s, CH_3Si), 0.42 [s, $Si(CH_3)_2$], 2.22 (s, 4-$CH_3C_6H_4$), 6.60 (d, $^3J_{HH}$ = 8.1 Hz, 2,6-H), 6.92 (d, 3,5-H). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ = –14.6 (CH_3Si), 2.5 [$Si(CH_3)_2$], 20.5 (4-$CH_3C_6H_4$), 121.5 (2-C), 124.8 (CCH_3), 131.0 (3-C), 155.5 (CN). – $^7Li\{^1H\}$ NMR (C_6D_6, 295 K): δ = –1.9. – Due to the extreme air sensitivity, a correct elemental analysis of **4b** could not be obtained.

4c: Yield 58%. – ^{1}H NMR (C_6D_6, 295 K): δ = 0.28 (s, CH_3Si), 0.58 [t, $^3J_{HH}$ = 7.6 Hz, CH_3CH_2O], 0.66 [s, $Si(CH_3)_2$], 2.19 (s, 4-$CH_3C_6H_4$), 2.81 (q, CH_3CH_2O), 6.84 (d, $^3J_{HH}$ = 8.2 Hz, 2,6-H), 6.93 (d, 3,5-H). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ = −14.9 (CH_3Si), 3.7 [$Si(CH_3)_2$], 13.9 (CH_3CH_2O), 20.5 (4-$CH_3C_6H_4$), 63.7 (CH_3CH_2O), 121.45 (C-2), 123.4 (CCH_3), 130.8 (C-3), 156.7 (CN). – $^7Li\{^1H\}$ NMR (C_6D_6): δ = 1.3. – $C_{36}H_{62}Li_3N_3O_2Si_4$ (702.1): calcd. C 61.59, H 8.90, N 5.99; found C 60.99, H 9.02, N 5.58.

4d: Yield 42%. – ^{1}H NMR (C_6D_6, 295 K): δ = 0.15 (s, $SiCH_3$), 0.30, 0.42 [s, $Si(CH_3)_2$], 0.74 [d, $^3J_{HH}$ = 6.2 Hz, $CH(CH_3)$], 3.97 [q, $CH(CH_3)$], 6.80–7.14 (m, C_6H_5). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ = −13.9 ($SiCH_3$), 3.2, 5.8 [$Si(CH_3)_2$], 27.6 [$(CH_3)CH$], 56.0 [$CH(CH_3)$], 124.6 (C-2,6), 126.8 (C-4), 130.7 (C-3,5), 153.5 (CN). – $^7Li\{^1H\}$ NMR (C_6D_6, 295 K): δ = −0.50. – $C_{31}H_{48}Li_3N_3Si_4$ (595.9): calcd. C 62.48, H 8.12, N 7.05; found C 62.30, H 8.56, N 6.89.

5) *Preparation of* $CH_3Si[Si(CH_3)_2N(4\text{-}CH_3C_6H_4)]_3TiX$ (X = Cl: **5a**; Br: **5b**): To a stirred solution of 1.20 g (2.23 mmol) of **3b** in 40 ml of pentane and 5 ml of diethyl ether which was cooled at −60°C was added 2.69 ml of *n*-butyllithium (2.5 M) in hexanes. The reaction mixture was warmed to room temp. and subsequently stirred for 2 h. The solution of the in situ-generated lithium amide **4b** was cooled to −60°C and 0.68 g of solid $TiCl_4(thf)_2$ [1.24 g (2.44 mmol) of $TiBr_4(thf)_2$] was added. After warming to room temp. over a period of 20 h and filtration through a G 3 frit the filtrate was concentrated to 10 ml and stored at −30°C. Compound **5a** precipitated as an orange, **5b** as a red crystalline solid (yields: 48% and 43%, respectively).

5a: M.p. 31°C (dec.). – ^{1}H NMR (C_6D_6, 295 K): δ = 0.20 (s, CH_3Si), 0.49 [s, $Si(CH_3)_2$], 2.05 (s, 4-$CH_3C_6H_4$), 7.00 (d, $^3J_{HH}$ = 8.3 Hz, 2,6-H), 7.08 (d, 3,5-H). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ = −13.8 (CH_3Si), 2.1 [$Si(CH_3)_2$], 20.8 (4-$CH_3C_6H_4$), 123.9 (C-2), 130.2 (C-3), 133.7 (CCH_3), 147.6 (CN). – IR (nujol): $\tilde{\nu}$ = 1490 cm^{-1} m, 1206 m, 884 m, 872 w, 846 m, 809 w, 795 w, 737 w, 718 w. – $C_{28}H_{42}ClN_3Si_4Ti$ (616.3): calcd. C 54.57, H 6.87, N 6.82; found C 54.28, H 7.10, N 6.58.

5b: M.p. 94°C. – ^{1}H NMR (C_6D_6, 295 K): δ = 0.19 (s, CH_3Si), 0.49 [s, $Si(CH_3)_2$], 2.05 (s, 4-$CH_3C_6H_4$), 7.00 (d, $^3J_{HH}$ = 8.1 Hz, 2,6-H), 7.16 (d, 3,5-H). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ = −13.6 (CH_3Si), 2.1 [$Si(CH_3)_2$], 20.8 (4-$CH_3C_6H_4$), 124.3 (C-2), 130.3 (C-3), 134.0 (CCH_3), 146.9 (CN). – IR (nujol): $\tilde{\nu}$ = 1601 cm^{-1} m, 1491 s, 1232 m, 1205 s, 1162 w, 1101 m, 1012 w, 932 w, 883 s, 868 s, 843 vs, 805 s, 792 s, 775 s, 735 m, 698 m. – $C_{28}H_{42}BrN_3Si_4Ti$ (660.8): calcd. C 50.89, H 6.41, N 6.36; found C 50.20, H 6.68, N 5.81.

6) *Preparation of* $CH_3Si[Si(CH_3)_2N(4\text{-}CH_3C_6H_4)]_3ZrCl$ (**6**): A solution of **3b** (3.68 g, 6.87 mmol) in 60 ml of diethyl ether was cooled to −78°C, and *n*-butyllithium (8.30 ml of a 2.5 M solution in hexanes) was added dropwise. The reaction mixture was allowed to warm slowly and was kept at 25°C for 2 h. After cooling to −78°C, solid $ZrCl_4$ (2.40 g, 10.3 mmol) was added and the reaction mixture warmed to room temp. over a period of 15 h. The solvent was removed in vacuo, the residue was extracted with 25 ml of toluene and the extract filtered through a G 3 frit. The solvent was subsequently removed in vacuo and the light-brown solid was washed with pentane (2 × 20 ml). Upon recrystallization from diethyl ether a yellow, microcrystalline solid was obtained. Yield 3.83 g (58%), m.p. 55°C (dec.). – ^{1}H NMR: δ = 0.23 ($SiCH_3$), 0.48 [$Si(CH_3)_2N$], 2.04 ($CH_3C_6H_4$), 6.96 (d, $^3J_{HH}$ = 8.2 Hz, 2,6-H), 7.06 (d, 3,5-H). – $^{13}C\{^1H\}$ NMR: δ = −15.9 ($SiCH_3$), 1.8 [$Si(CH_3)_2N$], 20.8 [$CH_3C_6H_4$], 126.1 (C-2,6), 130.9 (C-4), 133.8 (C-3,5), 143.2 (C-1). – IR (nujol): $\tilde{\nu}$ = 1492 cm^{-1} m, 1473 m, 1355 m, 1237 w, 1218 s, 1158 vw, 1085 m br, 1020 m, 938 w, 815 m, 872 w, 850 s, 796 vs, 766 w, 742 w, 708 w. – $C_{28}H_{42}ClN_3Si_4Zr$ (659.7): calcd. C 50.98, H 6.42, N 6.37; found C 51.03, H 6.65, N 6.48.

7) *X-ray Crystallographic Study of* **4a** *and* **5b**: Clear, colourless crystals of **4a** which had a prismatic habit and were suitable for X-ray crystallography were difficult to obtain (from pentane) and diffracted only poorly. A fairly regularly shaped single crystal was mounted under argon in a Lindemann capillary. A red block-shaped crystal of **5b** was mounted in a similar way. The X-ray diffraction data were collected on a Philips PW 1100 diffractometer with graphite-monochromated Mo-K_α radiation. Unit cell parameters were determined by a least-squares analysis of 25 automatically centred reflections in the range of $10° < \Theta < 15°$. Data were collected at 295 K in the range of $\Theta = 3–25°$ with a scan width of 0.80° by using a technique described previously[18]. An empirical absorption correction using the program DIFABS (N. Walker, D. Stuart, *Acta Crystallogr., Sect. A*, **1983**, *39*, 158) was applied, and the data were corrected for Lorentz and polarization effects. The intensities of three representative reflections were measured every 5 h of X-ray exposure time; they remained constant throughout the data collection indicating crystal and electronic stability (no decay correction was applied). Neutral atom scattering factors were taken from D. T. Cromer, J. T. Waber, *International Tables of X-Ray Crystallography*, The Kynoch Press, Birmingham, **1974**. Crystal data of **4a**: $C_{19}H_{48}Li_3N_3Si_4$, orthorhombic, space group $cmc2_1$, a = 17.154(3), b = 11.671(3), c = 15.380(3) Å, V = 3079.14 Å^3, Z = 4, $F(000)$ = 992, ρ_{calcd} = 0.975, μ(Mo-K_α) = 2.0 cm^{-1}, R = 0.093, R_w = 0.1001, N = 696. – Crystal data of **5b**: $C_{19}H_{48}BrN_3Si_4Ti$, monoclinic, space group $2_1/n$, a = 10.677(3), b = 18.512(4), c = 17.822(4), β = 95.94(2)°, V = 3503.65 Å^3, Z = 4, $F(000)$ = 1376, ρ_{calcd} = 1.253, μ(Mo-K_α) = 15.2 cm^{-1}, R = 0.0630, R_w = 0.0633, N = 1623. – The data analysis and refinement were carried out with the programmes of the SHELX 76 software package[19]. The relatively poor quality of the crystals of **4a** resulted in relatively high esd's on all parameters but the main features of the structure are well established. The structure was solved by direct methods. The co-ordinates of the metal atoms in **5b** were deduced from a Patterson synthesis. The remaining non-hydrogen atoms in both structures were located from subsequent difference Fourier syntheses and refined with anisotropic thermal parameters. The positions of the hydrogen atoms were located in electron density difference maps and were included in the structure factor calculations with thermal factors of 0.08 Å^2, but their parameters not refined[20].

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